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14. ABSTRACT SRI International (SRI) has conducted a detailed study of localized hydrocarbon/hydrogen plasmas for the purpose of depositing diamond thin films near atmospheric pressure and at low temperature. A microhollow cathode device was utilized to generate localized plasmas which were characterized spectroscopically. In addition, the electron density of these plasmas was predicted through computer generated simulations.					
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Microhollow Cathode Plasmas for Low Temperature, Ambient Diamond Growth

### ABSTRACT

SRI International (SRI) has conducted a detailed study of localized hydrocarbon/hydrogen plasmas for the purpose of depositing diamond thin films near atmospheric pressure and at low temperature. A microhollow cathode device was utilized to generate localized plasmas which were characterized spectroscopically. In addition, the electron density of these plasmas was predicted through computer generated simulations.

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DCMA Lathrop (S0507A)  
P.O. Box 232  
700 E. Roth Road, Bldg. 330 (Lathrop, CA)  
French Camp, CA 95231-0232

Dr. Brian Holloway  
Defense Sciences Office/Strategic Technology Office  
Defense Advanced Research Projects Agency  
3701 N. Fairfax Drive  
Arlington, VA 22203-1714

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**Technical Point of Contact:**  
Dr. Christine Cuppoletti  
Polymer Chemist II  
SRI International  
333 Ravenswood Avenue  
Menlo Park, CA 94025  
Telephone: (650) 859-4967  
Fax: (650) 859-4321  
Email: christine.cuppoletti@sri.com

**Administrative Point of Contact:**  
Ms. Valerie Reedich  
Sr. Contract Administrator  
SRI International  
333 Ravenswood Avenue  
Menlo Park, CA 94025  
Telephone: (650) 859-4694  
Fax: (650) 859-2829  
Email: valerie.reedich@sri.com

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333 Ravenswood Avenue • Menlo Park, California 94025-3493 • 650.859.2000 • [www.sri.com](http://www.sri.com)

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## **MICROHOLLOW CATHODE PLASMAS FOR LOW TEMPERATURE, AMBIENT DIAMOND GROWTH**

Final Report By: Christine Cuppoletti

Contributors: Colby Bellew, Mark Tinkle, and Robert Robertson

### **A. EXECUTIVE SUMMARY**

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SRI International has conducted a detailed study of localized hydrocarbon/hydrogen plasmas for the purpose of depositing diamond thin films near atmospheric pressure and at low temperature. We were successfully able to generate localized plasmas having the active species necessary and favorable for diamond growth utilizing a needle plate configuration. Utilizing these parameters, similar plasmas were generated from a microhollow cathode design. However, these devices could not sustain the plasma for any extended length of time (<10-20 sec) as the devices fell to high leakage currents due to breakdown of the dielectric layer in the cavity design. Supplementary information was gained through computer simulations completed to predict the electron density of a sustained microplasma. These simulations show that, although the electron density of these plasmas would be exceptionally high ( $10^{21}\text{m}^{-3}$ ), the resulting plasma frequency of 0.3 THz still allows for through-plasma laser activation of growth species. Given these findings, it is our conclusion that, with further development of the microhollow cathode design, these structures would support localized thin film diamond growth near atmospheric temperature and pressure.

### **B. TECHNICAL APPROACH**

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Current methods for diamond thin film synthesis require high temperature and vacuum and are incompatible with controlled deposition on low temperature substrates. This project set out to address these issues through an investigation of microplasmas. Microplasmas are generated with a microhollow cathode and have the potential to eliminate bulk substrate heating ( $>200\text{C}$ ), allow for deposition at atmospheric pressure, and enable localized diamond thin film growth. Lower temperatures would allow for deposition onto alternative substrates while the activation energy for nucleation could be supplied via efficient localized coupling and/or laser-activation. Deposition near atmospheric temperature and pressures would minimize the presence of non-diamond carbon phases.<sup>1</sup> Furthermore, the microhollow cathode design, while localized, would still achieve sufficient plasma species density and can be fabricated in any number of patterns or arrays to produce specified designs or continuous films.

The growth of diamond thin films is controlled primarily by the ratio of  $\text{CH}_3$ ,  $\text{C}_2$ , and H radicals.<sup>1</sup> These radicals have characteristic emission spectra that will enable us to determine their relative abundance in the localized plasma. Their energies are indicated in the emission spectrum of a microwave-generated plasma optimized for diamond growth, shown in Figure 1.<sup>2</sup> The primary growth species for diamond thin films was determined to be the carbon dimer,  $\text{C}_2$  radical, whose excited state emission is at 5165 Angstroms. It has been shown that an increase in the intensity of this peak was correlated with an increase in the rate of diamond growth. Other species of interest are hydrogen at 6560 Angstrom, CH at 4414 Angstroms, and argon at 7504 Angstroms.

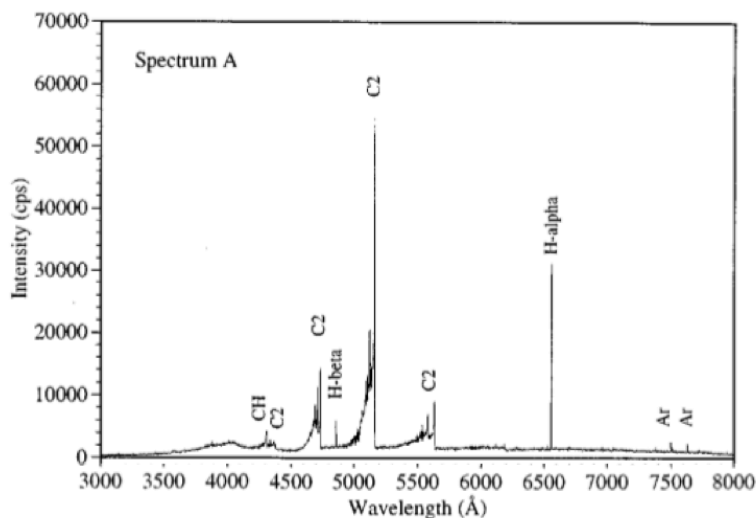


Figure 1: Ref. plasma emission spectrum identifying the presence and respective ratios of radicals shown to be favorable for diamond growth indicating the emission peaks of the primary radicals for diamond growth: C2 – 5165, H – 6560, and CH – 4314 Angstroms (from ref 2).

Figure 1 shows the emission of a plasma shown to grow diamond films. We will use these peaks as markers indicating when we have generated a plasma from the microhollow cathode that is suitable for growth of diamond thin films.

Microhollow cathodes have been reported to generate plasmas at near atmospheric pressures, primarily in argon.<sup>3</sup> The microhollow cathode consists of a hollow cavity formed by a silicon cathode, dielectric, and metal anode, as illustrated in Figure 2. The source geometry determines the optimum operating pressure with diameters of 10-100  $\mu\text{m}$  supporting plasma generation at atmospheric pressures. A flow through design utilizes ion optics and directs the active species toward the substrate and enables the possibility of utilizing through-plasma laser activation. Previous investigations at SRI have demonstrated that these cavities generate argon plasmas under DC pulsed power of approximately 200 V and  $\mu\text{A}$ -mA currents. Furthermore, the cavities allow for the microscale confinement of the plasma, minimizing plasma-induced substrate heating, while the flow through design enables localized deposition.

This project aimed to utilize these advantages of the microhollow cathode to grow diamond thin films near atmospheric pressure and without substrate heating. The process for device fabrication having already been developed, it was simply a matter of testing the device with other gases and understanding the processing parameters required to generate a diamond growth plasma. The benchmark for this effort was a plasma emission spectrum

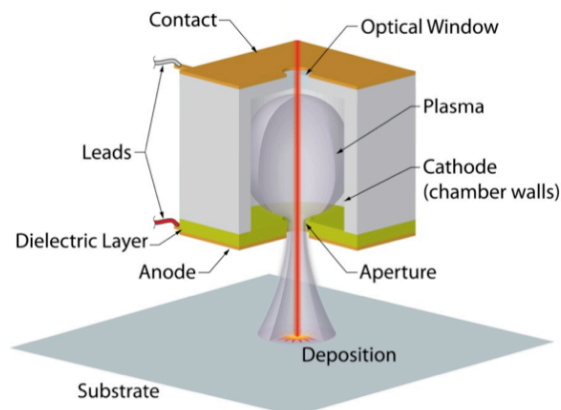


Figure 2: Microhollow Cathode device structure. The through cavity design utilizes ion optics and also allows for the optional use of laser activation either within the plasma or at the substrate.

similar to that in Figure 1.

SRI was charged with the following four tasks to achieve this objective. The first was to determine the operating parameters necessary to generate diamond growth plasma using a needle-plate configuration. This configuration was chosen as a step toward generating a confined plasma but with a simplified electrode geometry. Meanwhile, in Task 2, the microhollow cathodes were fabricated. Task 3 involved the generation of a diamond growth plasma utilizing the microhollow cathode devices and the characterization of plasma properties. The final task was to determine the feasibility of the incorporation of a laser assisted plasma process into the design.

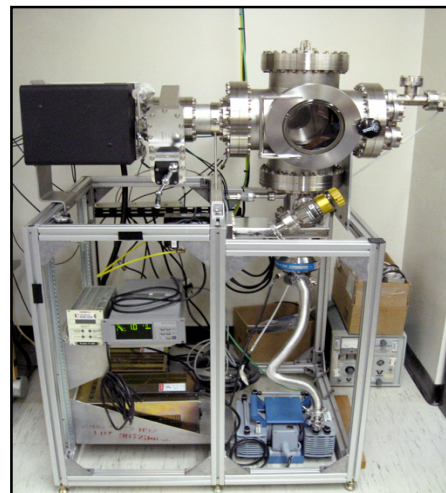


Figure 3. The vacuum chamber at SRI where localized diamond growth plasma experiments were conducted.

## C. RESULTS

### Task 1: Initial plasma generation

As a first step to determine the conditions required to generate a localized microplasma suitable for diamond growth, a metal needle-plate electrode configuration was utilized. This configuration models a localized plasma and begins the process of establishing chamber process parameters.

**Experimental Setup:** The vacuum system is shown in Figure 3 to the right. Within this chamber, a tungsten needle was mounted at a distance of 8 mm above an aluminum plate. The needle was connected via feed-throughs to a Bertan Associates model 205A-05R high voltage power supply and 116 k $\Omega$  current limiting resistor. The plate was grounded. To collect the emission spectrum of the generated plasma, an optical fiber was mounted perpendicular to the gap between the needle-plate electrodes at a distance of about 2 cm and fed through to an Ocean Optics spectrometer. The chamber had a base pressure of  $10^{-8}$  Torr and was plumbed with hydrogen, methane, and argon gasses.

All experiments were conducted under closed chamber conditions. The chamber was evacuated, filled with the process gases, and then closed to both the vacuum and gas inlets. This approach eliminated the need to determine gas flow rates and was sufficient due to the low rate of gas consumption upon plasma generation. This was verified by the lack of change in pressure readings during the course of the plasma generation and characterization. The key recorded parameters were the partial pressures of the process gases, the total pressure, applied bias, and finally the current at which a plasma could be sustained. Once a plasma was generated, the emission spectrum was used to characterize the component species.

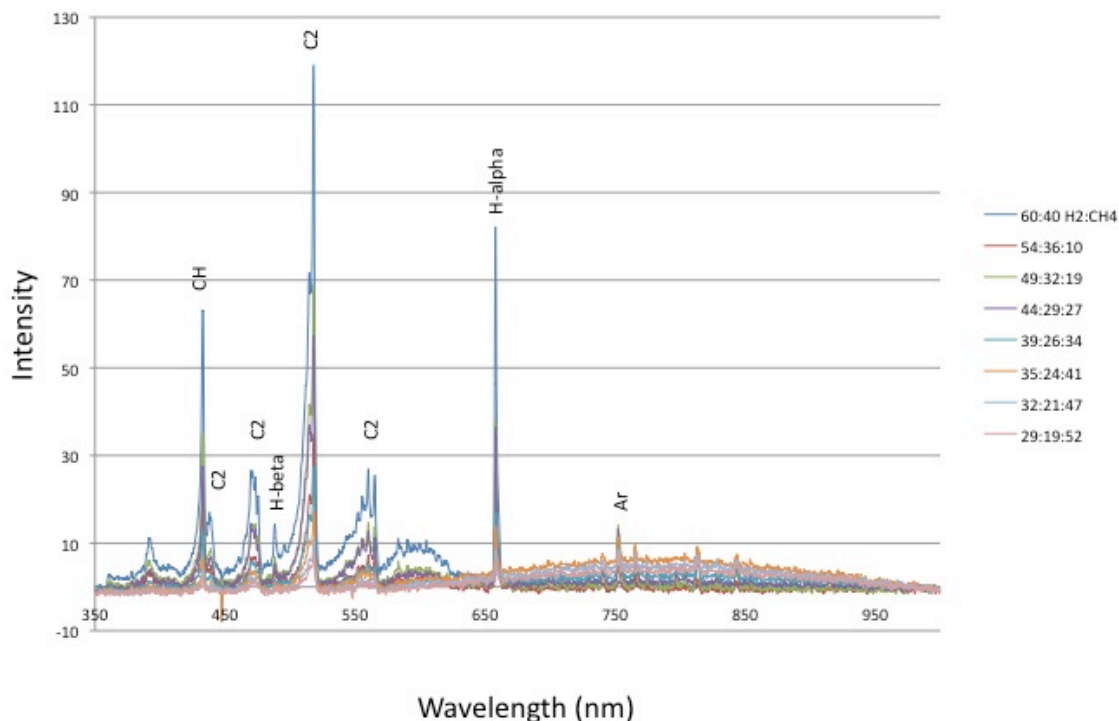


Figure 4. Emission spectra of needle-plate plasma, primary species labeled. The spectra are of plasma generated in the presence of increasing concentration of argon in the system. The total pressure was maintained at 100 torr for all measurements and the spectra were collected from plasma under the applied bias of 700V and currents of 2-3 mA.

Figure 4 shows the emission spectra of plasma generated at a pressure of 100 Torr, 700 V, and currents of 2-3 mA. These particular spectra were gathered to determine optimum argon levels in the chamber. We were interested in introducing argon into the system since literature reports indicated that the presence of argon in conventional plasma deposition of diamond enhanced the production of the carbon growth species (C<sub>2</sub>).<sup>2</sup> However, we found that the microplasma generated in our system did not result in an increase in C<sub>2</sub> emission. We determined that the presence of argon in the chamber did not enhance the presence of key diamond growth species and instead displaced them with a broad emission around the argon peaks.

We also conducted experiments to determine the optimum ratio of hydrogen to methane and resulted in a 3:2 ratio of hydrogen to methane as shown in the first blue spectrum of Figure 4. This concentration of methane was required in order to produce the intense C<sub>2</sub> emission indicated as being necessary for diamond growth. The peak emissions of the key diamond growth species are labeled in Figure 4 and are in good correlation with literature findings (shown in Figure 1). It should be noted that the relative ratio of hydrogen to methane required to produce this emission differs dramatically from that required to produce similar emission spectra in conventional plasma systems in which the methane fraction is just 2% in hydrogen. We are unable to account for the reason for this difference at this time, but felt satisfied that the processing parameters required for the generation of a confined diamond growth plasma had been determined experimentally.

## Task 2: Microhollow cathode fabrication

Microhollow cathode sources were fabricated using silicon MEMS processing at SRI's microfabrication facility. Twelve chips were fabricated on a single 100 mm Si (100) wafer. The chips had 1, 2, 4, or 16 cavities as shown in Figure 5. The diameter of the cavities tested in this study was 50  $\mu\text{m}$ .

The process steps were as follows:

Wafer: 100 mm N-type/Phos Si (100), DSP, +/-15  $\mu\text{m}$

1. Pattern backside on ASML
  - Global ASML marks, crosses alignment, labels
2. Etch marks into backside Si, depth 2000  $\text{\AA}$ 
  - RIE, Plasmatherm
3. Deposit frontside dielectric
  - SiON, STS PECVD, 5  $\mu\text{m}$  thick
4. Deposit frontside metal
  - TiW/Ni, MRC sputter, 2500  $\text{\AA}$  thick
5. Pattern large frontside metal pads
  - Contact mask
  - Aligned to ASML marks on backside
6. Etch metal pads
  - Wet etch / RIE
7. Pattern frontside holes
  - 7  $\mu\text{m}$  photoresist, ASML stepper, aligned to marks on backside
  - Single holes or arrays (see pg 1), crosses, labels
8. Etch frontside holes
  - Etch metal: wet etch / RIE
  - Etch SiO<sub>2</sub>: RIE, Plasmatherm
  - Etch Si: DRIE, Alcatel. Depth: 100  $\mu\text{m}$
9. Deposit backside metal
  - TiW/Ni, MRC sputter, 4000  $\text{\AA}$  thick
10. Pattern backside
  - Contact mask
  - Large access holes (~6 mm diameter), dicing lanes
11. Etch backside holes
  - Etch metal: wet etch / RIE
  - Etch Si: DRIE, Alcatel. Depth ~335  $\mu\text{m}$  to create thru holes
12. Cleave samples along DRIE dicing lanes
13. Clean

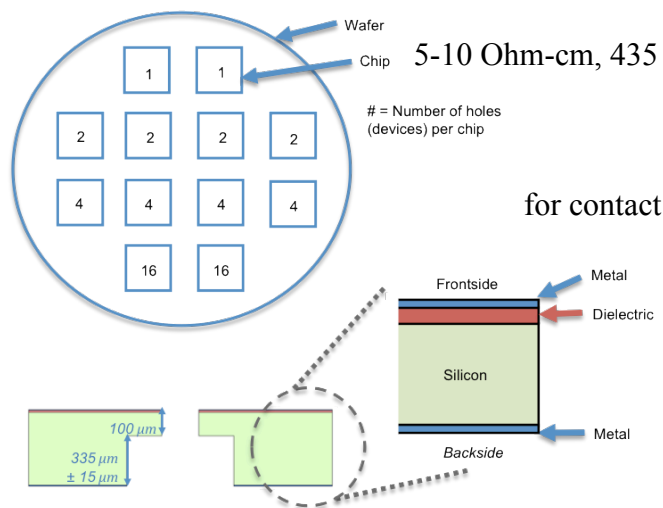
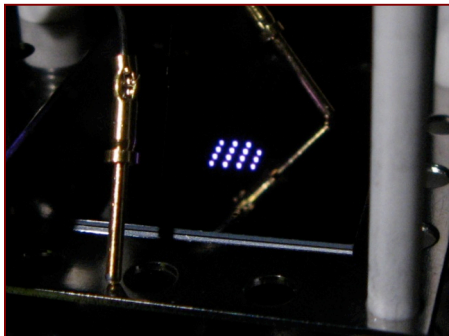


Figure 5. Wafer layout for the production of 12 chips having 1, 2, 4, and 16 holes and a cross-section of the microhollow ...

### Task 3: Microplasma diagnostics

Working from the process parameters established in Task 1, we replaced the needle-plate electrodes and generated diamond growth plasma utilizing the microhollow cathode devices. The plasma generated had similar spectral character as that formed in Task 1 but due to breakdown of the devices, had very limited lifetimes. Even with the addition of the 116 k $\Omega$  current limiting resistor, the longest lasting plasmas were just tens of seconds while the majority of the devices failed after just a few seconds of operation. Device failure was defined as high leakage currents requiring higher applied voltages to generate a plasma and a subsequent failure to produce a plasma at all. This behavior is indicative of a breakdown of the dielectric layer because of excessive currents across the device. We believe that this issue can be resolved through use of a thicker dielectric layer and further limiting the current across the device. However, iteration of the device structure was outside the scope of this project and could not be addressed at this time.



**Figure 6.** Photograph of plasma emission generated from 4x4 microhollow cathode array in 100 torr of a 50:50 methane:hydrogen mix.

During the brief period that the devices generated a plasma, we were able to capture the spectra of and photograph (see Figure 6) the generated plasma but found the system was simply too unstable to gather further information of any significance related to the electron density, temperature, or mass-spec. These measurements require a stable plasma to be maintained for a minimum of several minutes, and at least twenty in the case of the Langmuir probe measurement used to establish the electron density. However, the plasma emission did intermittently appear to be similar to that recorded in Figure 4; having the characteristic C2, CH, and H emission. This leads us to believe that more robust devices would be capable of generating plasma suitable for

thin film growth of diamond films.

### Task 4: Feasibility of laser-assisted plasma process

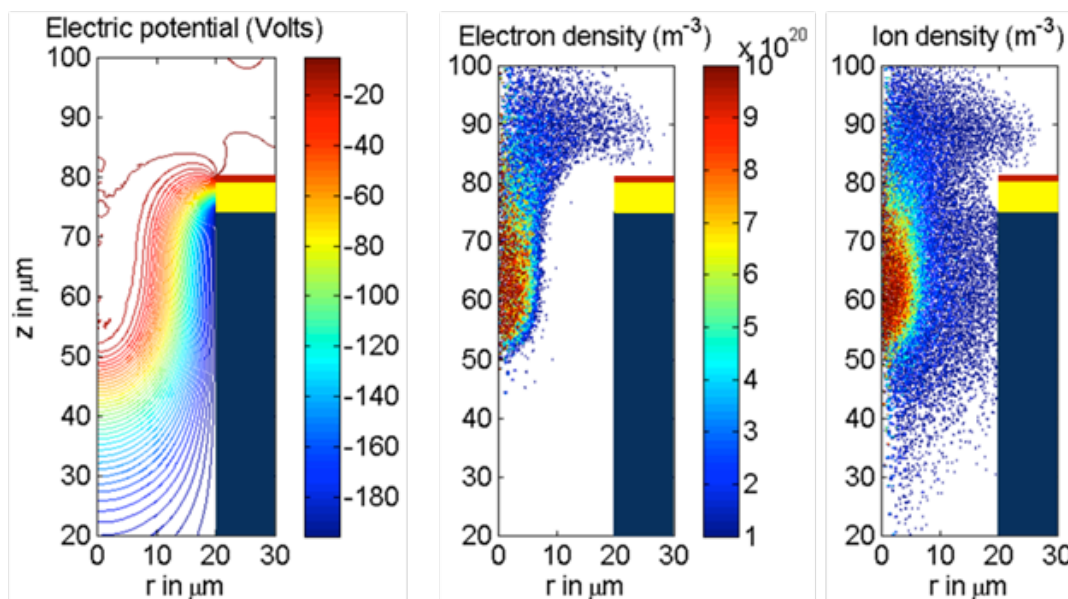
The microhollow cavity design was evaluated to determine if the confined plasmas were compatible with the use of a thru-plasma laser for potential laser-assisted thin film growth processes. The primary concern was whether or not the potentially high electron densities of the confined plasma and correlated plasma frequency would prevent laser penetration via Debye shielding or free electron reflection.

In conventional delocalized plasmas, the electron density is determined through the use of a Langmuir probe mounted inside the plasma chamber. From within the plasma, the electron density is determined by measuring the current over a known probe area. However, to obtain a physically meaningful measurement, the area of the probe must be insignificant with respect to the plasma volume so that it does not alter the plasma in the process of analyzing it. In a microplasma, this becomes non-trivial and is not feasible to accomplish with a conventional Langmuir probe, as the probe area is much larger than that of the plasma. Given this dilemma, we sought to determine the electron density through modeling of the microhollow cathode.



SRI has extensive experience modeling the electron density of plasmas generated by microhollow cathodes. In lieu of experimental verification due to the physical constraints of the measurement in addition the rapid failure of the devices produced in this study, we turned to these simulations to predict the feasibility of incorporating a laser-assisted process in a robust microhollow cathode system. These simulations demonstrate that, although exceptionally high, the plasma densities are not such that one would expect debye shielding to be an issue when attempting to penetrate a confined microplasma with either visible or IR lasers.

Computer simulations of plasma generation in the cavity structure allow us to gain a general sense of the probable electron densities. Although these simulations are for idealized conditions and a simplified gas, we feel that they give us a reasonable estimate of the electron densities that can be expected in the confined microplasma and alleviate concerns that laser penetration will be an issue. Figure 7 shows an OOPIC simulation carried out at SRI and constructed to evaluate device operation at the 10  $\mu\text{m}$  scale and to carry a preliminary analysis of sheath structure, plasma velocity distributions, and cavity potentials. This tool allows us to simulate, evaluate, and optimize the performance of each demonstration component. In this example, ion densities of order  $10^{21} \text{ m}^{-3}$  are achieved in hollow cathode mode in 200 Torr of argon with a 2 mA discharge current. These parameters represent the extreme upper end of the operating conditions for the microhollow cathode, and in fact, we found experimentally that such currents are too high to be supported for a sustained period of time by the device. The modeled cathode inner diameter is 40  $\mu\text{m}$ , with a 5  $\mu\text{m}$  dielectric separating it from the anode film. The potential contours show that the plasma is acting as a virtual anode inside the cathode cavity. Comparing electron and ion density contours, we see ions streaming across a relatively thick sheath toward the cathode, where the secondary emission coefficient is 3%. The plasma developed in 200 ns from 300 V applied to a significant seed density ( $10^{16} \text{ m}^{-3}$  to avoid stochastic time delay), after which the potential was reduced to 200 V.



**Figure 7:** Particle-in-cell simulation of plasma device operation, showing (a) cavity potential, (b) electron and (c) ion distributions, after device turn-on. The device and plasma are radially symmetric about the z-axis.

Table 1 lists the frequencies over a range of the electromagnetic spectrum and the associated electron density as calculated from the relationship that the frequency of the plasma (in Hz) is approximated as 8980 times the square root of the electron density.<sup>4</sup> We assume that laser activation of the plasma or the surface would utilize frequencies within the visible to infrared range of the spectrum. Table 1 shows the electron densities that would be required within the plasma to cause free electron reflection.

**Table 1. Plasma Frequency and Electron Density**

Class	Frequency	Wavelength	Electron Density
Vis/Near IR	300 THz	1 mm	$1^{21} \text{ cm}^{-3}$
Far IR	3 THz	100 mm	$1^{18} \text{ cm}^{-3}$
Radio (VHF)	300 MHz	1 m	$1^8 \text{ cm}^{-3}$

The modeling results showed that we would expect electron densities of  $10^{21} \text{ m}^{-3}$ , or  $10^{15} \text{ cm}^{-3}$  to be possible in plasma generated with the microhollow cathode. As this is a full three to six orders of magnitude less than the density required for Debye shielding in the vis-IR, our conclusion is that penetration of the plasma with a vis-IR laser should not be a problem.

## D. CONCLUSIONS AND RECOMMENDATIONS

The microhollow cathode is a promising device for the generation of localized plasma. The localized, atmospheric pressure, low (substrate) temperature technique has the promise to be compatible with thin film growth strategies such as:

- Pulsed laser-assisted process to enhance surface reactions
- Precursor selection: oxygen, halogens
- Substrate biasing
- Integrated ion optics
- Substrate selection
- Surface pretreatment

The primary issue with these devices is the breakdown of the dielectric layer at high currents. This could potentially be solved by the addition of a larger current limiting resistor, making the dielectric thicker, and/or using more robust materials. The devices that were tested in this study were not able to sustain plasma for more than a few seconds due to breakdown of the dielectric at high currents, which exceeded 5 mA when plasma generation was achieved. A sustained plasma would be required to grow a thin film from active species within the plasma.

From our simulations in an idealized system, we would not expect that penetration of the plasma with a laser would be a problem. The electron densities predicted within the microhollow



cathode are well below what would be required for free electron reflection to become an issue at Vis – IR frequencies.

We are encouraged that ratios of plasma species are in line with the known process window for diamond thin film growth. We would recommend further development of the microhollow cathode for the generation of diamond growth plasmas utilizing a thicker dielectric layer and taking extra precautions to limit the current across the device to less than 5 mA. A more robust device would enable proper characterization and further optimization of the plasma for diamond thin film synthesis.

## **E. BIBLIOGRAPHY**

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<sup>1</sup> Das, D., Singh, R. N. “A review of nucleation, growth and low temperature synthesis of diamond thin films” *International Materials Reviews* (2007) 52(1), 29-63.

<sup>2</sup> Gruen, D. M., Zuiker, C. D., Krauss, A. R., Pan, X. “Carbon dimer, C<sub>2</sub>, as a growth species for diamond films from methane/hydrogen/argon microwave plasmas” *J. Vac. Sci. Technol. A* (1995) 13(3), 1628-32.

<sup>3</sup> Schoenbach, K. H., El-Habachi, A., Shi, W., and Ciocca, M. “High-pressure hollow cathode discharges” *Plasma Sources Sci. Technol.* (1997) 6, 468-77.

<sup>4</sup> Brown, Ian G. The Physics and Technology of Ion Sources, Second Edition. Wiley-VCH Verlag GmbH & Cco. KGaA, 2004, pg 16.